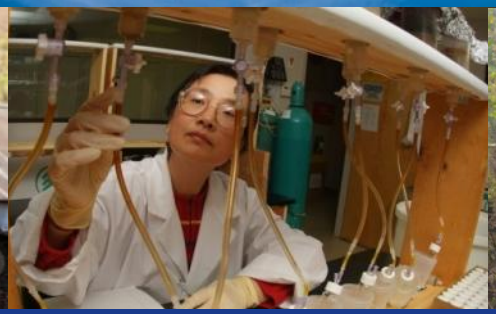



Field-Scale Treatability Study for Enhanced In Situ Bioremediation of Explosives in Groundwater: BioBarrier Installation and Hot Spot Treatment Using DPT Injection

May 24, 2012

Steven T. Downey, PE, PMP
The Shaw Group
Richard Meadows
USACE, Huntington

Shaw® a world of Solutions™

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
24 MAY 2012		**00-00-2012 to 00-00-2012**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Field-Scale Treatability Study for Enhanced In Situ Bioremediation of Explosives in Groundwater: BioBarrier Installation and Hot Spot Treatment Using DPT Injection	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **U.S. Army Corps of Engineers,Huntington District,502 Eighth Street,Huntington,WV,25701-2070**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
Presented at the NDIA Environment, Energy Security & Sustainability (E2S2) Symposium & Exhibition held 21-24 May 2012 in New Orleans, LA.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**44**	

Agenda

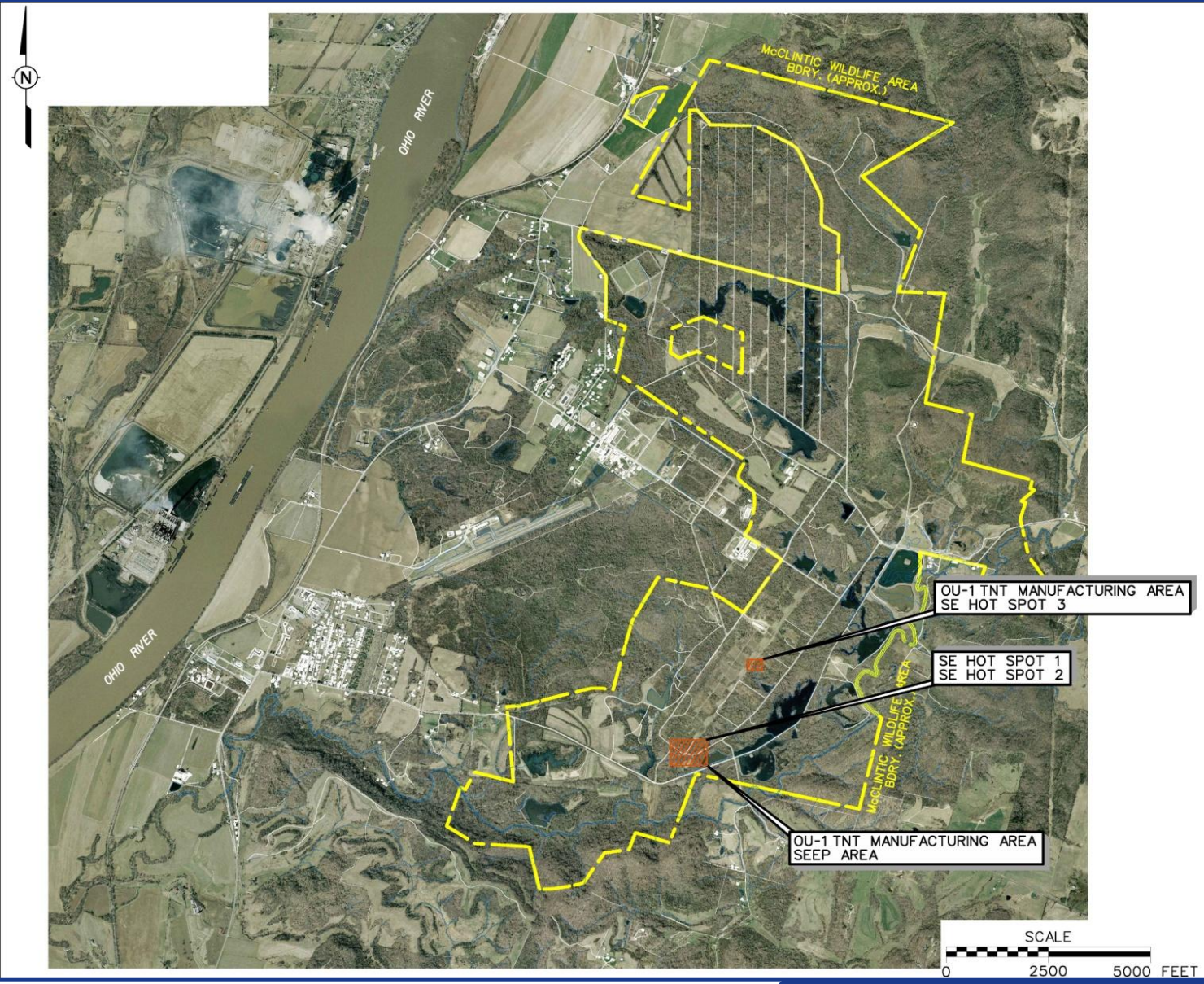
- Introduction
- Technology Description
- Carbon Source Comparison
- BioBarrier
- SE Hot Spot 1
- SE Hot Spot 2
- SE Hot Spot 3
- Conclusions

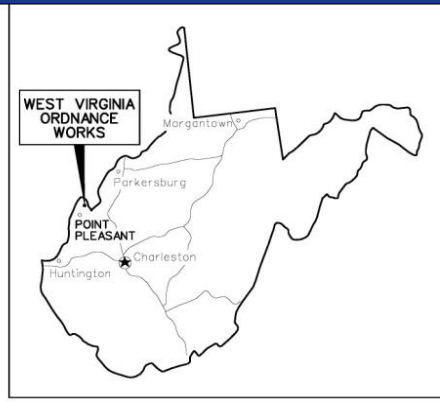
Introduction

- West Virginia Ordnance Works (WVOW) was a TNT manufacturing facility from 1942-1945
- The WVOW site is located on the east bank of the Ohio River, six miles north of Point Pleasant, WV
- WVOW included 12 TNT production lines
- TNT production resulted in soil and groundwater contamination
- Complete decontamination was not achieved, so portions were transferred to the state of West Virginia for use as a wildlife management reserve
- The site is now the McClintic Wildlife Management Area

WVOW TNT Manufacturing Area

WVOW TNT Manufacturing Area





LEGEND

EISB GROUNDWATER STUDY AREAS

FIGURE 1-1
SITE LOCATION MAP

THE EISB TREATABILITY STUDY WORK PLAN
WEST VIRGINIA ORDNANCE WORKS
MASON COUNTY, WEST VIRGINIA

Shaw® a world of Solutions™

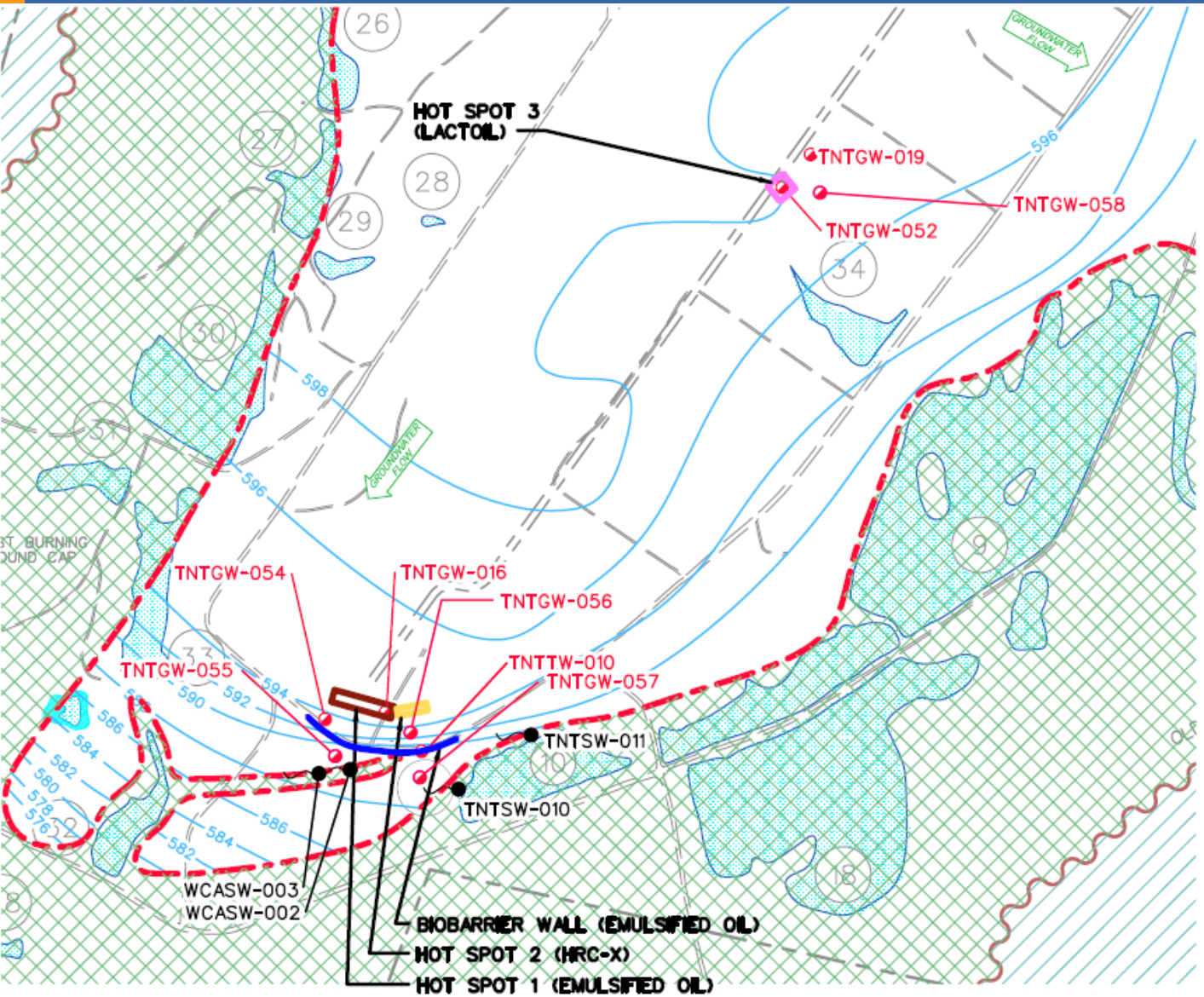
Introduction (continued)

- Four study areas; Seep Area, SE Hot Spot 1, SE Hot Spot 2, and SE Hot Spot 3
- Primary chemicals of concern (COCs) include: 2,4,6-Trinitrotoluene (TNT), 2,4-Dinitrotoluene (2,4-DNT), 2,6-DNT, 2-Amino-4,6-DNT (2ADNT), and 4-Amino-2,6-DNT (4ADNT)
- Enhanced in situ bioremediation (EISB) was selected for field-scale evaluation
- Three different carbon sources are being compared for their effectiveness: SRS™ -Emulsified Vegetable Oil (Terra Systems, Inc.), HRC-X™ (Regenesis), and LactOil™ (JRW)
- The study is focused only on groundwater treatment

Introduction (continued)

- Baseline sampling was performed prior to injection of the carbon source in the study areas
- Nine wells and four seep locations were sampled
- Performance sampling was conducted quarterly after injection for one year followed by the first of two semi-annual sampling events
- One remaining semi-annual sampling event is planned for the end of August 2012
- A comprehensive evaluation report will be prepared at the conclusion of the study

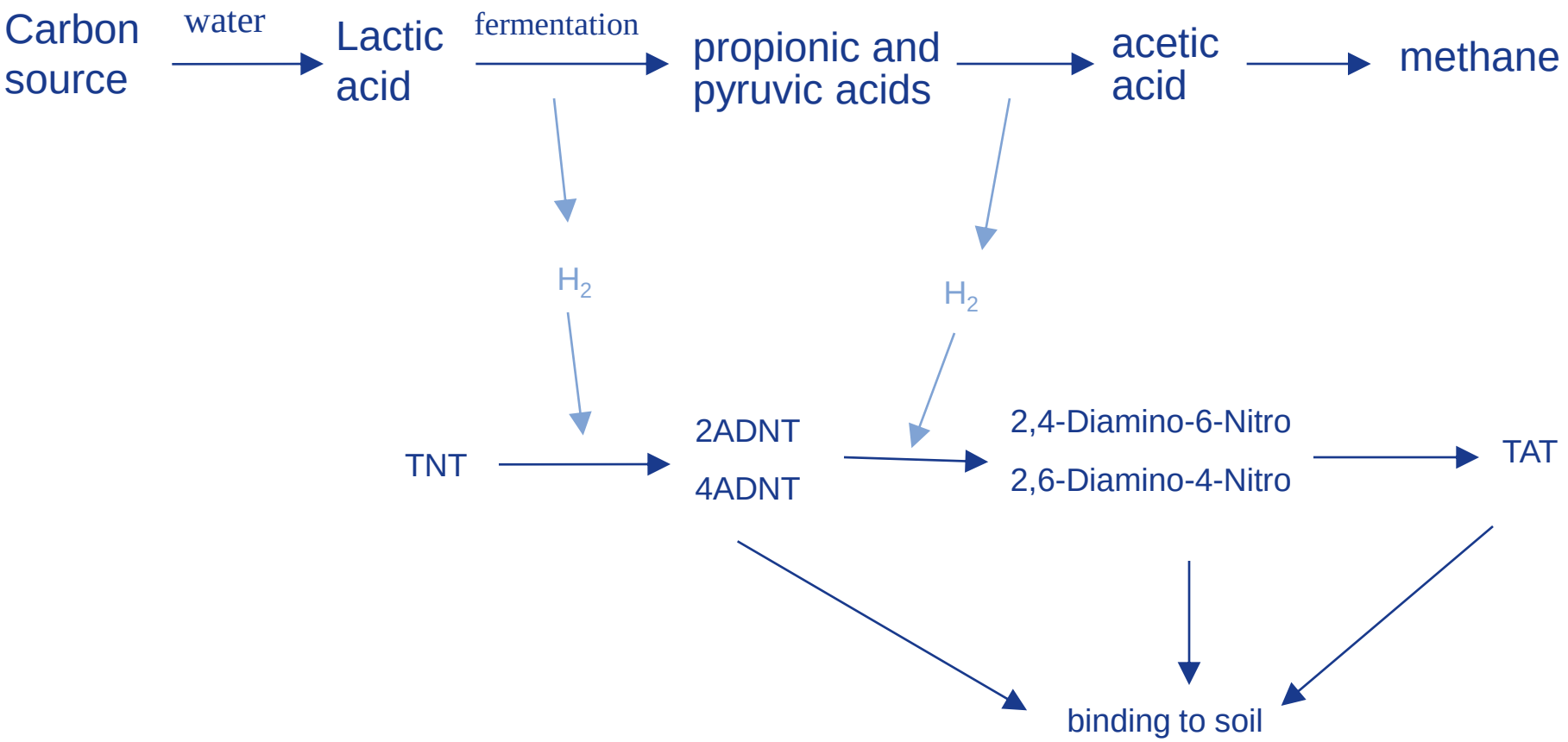
WVOW TNT Treatability Study Area



Technology Description

- EISB is a process where a reducing environment is created for indigenous microorganisms
- A carbon source is injected into the aquifer, which provides an energy source for indigenous microorganisms
- As carbon is consumed, O_2 is depleted until the system becomes anaerobic
- After O_2 is consumed, anaerobic fermentation begins and H_2 is released into the system
- H_2 is consumed in competing reactions – reduction of electron acceptors and reduction of nitroaromatics

Carbon Source Degradation and TNT Biodegradation Pathway



Carbon Sources Used

- SRS, Emulsified Vegetable Oil was used for the Seep Area (BioBarrier) and SE Hot Spot 1
- HRC-X was used for SE Hot Spot 2
- LactOil was used for SE Hot Spot 3

Carbon Source – SRS

- SRS, Emulsified Vegetable Oil
  - SRS is a slow release substrate comprised of a mixture of emulsified oil (50-70%) and sodium lactate (< 5%) manufactured by Terra Systems, Inc.
  - Fast-release lactate creates reducing conditions soon after injection to kick-start the bioactivity
  - Emulsified oil dissolves slowly, releasing hydrogen to maintain reducing conditions, providing a longevity of three to five years
  - Emulsified oil is immobile after adsorbing to soil particles
  - SRS has the consistency of milk and comes ready for injection
  - Applied at the Seep Area to form long lasting BioBarrier and at SE Hot Spot 1, which has a high groundwater flow velocity

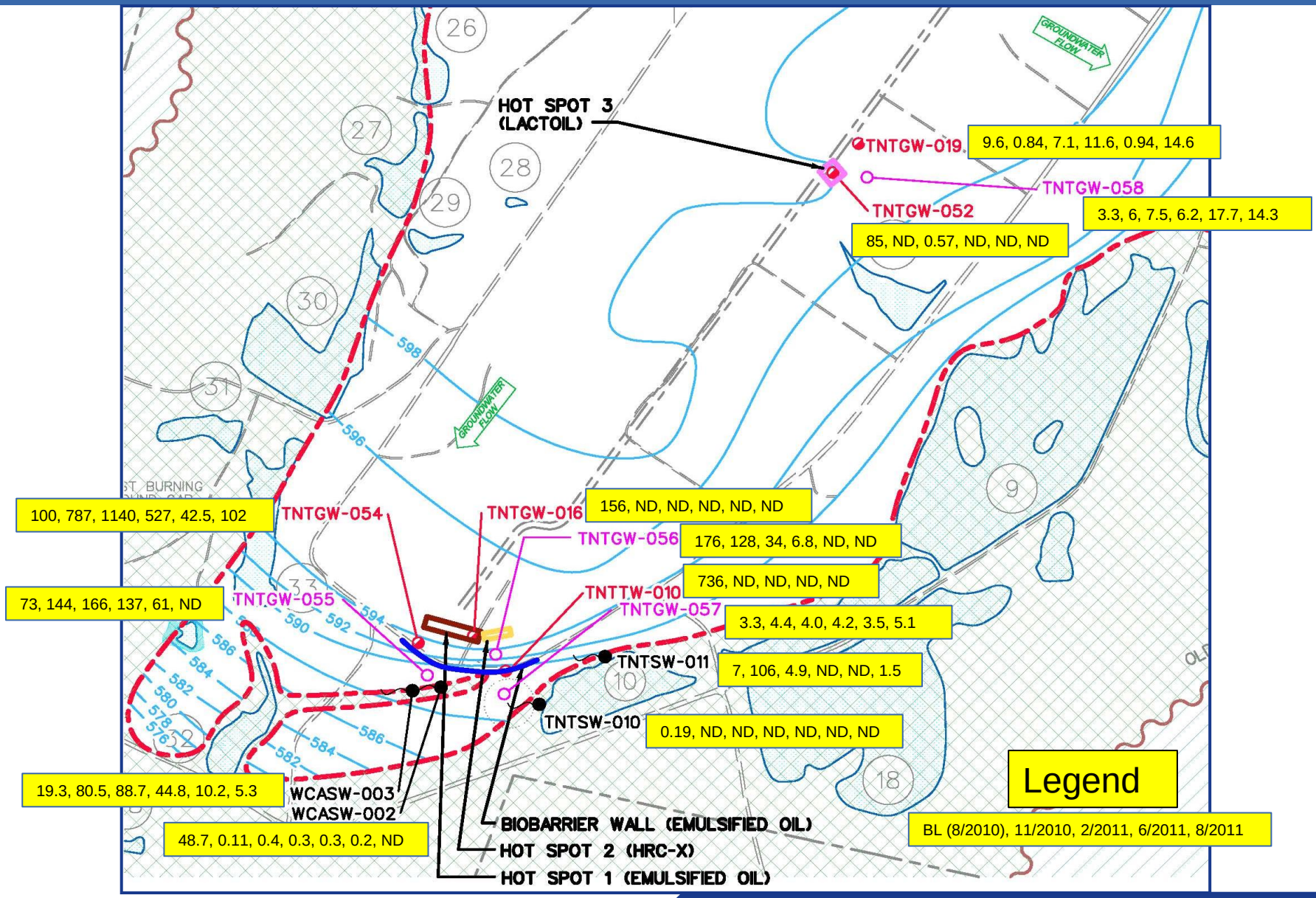
Carbon Source – HRC-X

- Hydrogen Release Compound (extended release formula)
  - A proprietary polylactate ester manufactured by Regenesis Bioremediation Products, Inc.
  - A viscous material that slowly releases lactic acid
  - High viscosity at ambient temperature – needs to be heated for injection
  - Relatively immobile and does not migrate; ideal for aquifers with steep hydraulic gradients and/or high flow velocities
  - Extended release formula remains active for multiple years
  - Applied at SE Hot Spot 2, which has a high groundwater flow velocity
  - Provides a side-by-side comparison with SRS at SE Hot Spot 1

Carbon Source – LactOil

- LactOil
  - A mixture of ethyl lactate (40%) and vegetable oil (40%) manufactured by JRW
  - Ethyl lactate generates more metabolic acids per unit weight than sodium lactate. It has the potential to reduce pH, thus requiring pH buffering
  - One micrometer oil droplet compared to 5-10 micrometers in common emulsified oil, moves through pore space more easily, but also has a shorter active life
  - Applied at SE Hot Spot 3 where COC concentrations are lower and longevity is not as critical

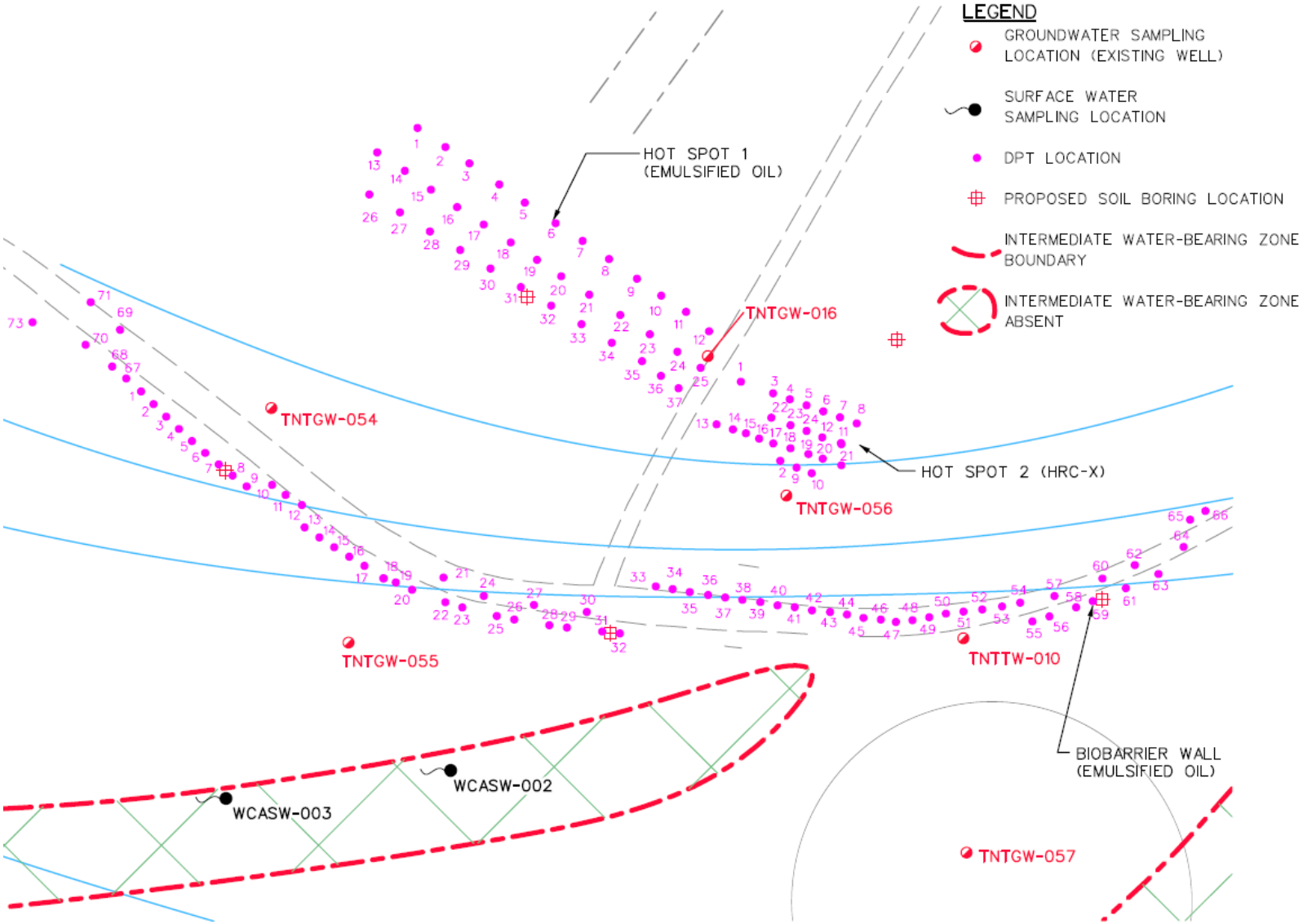
TNT Concentration Trends to Date



Seep Area – BioBarrier Installation

- SRS injected in a linear pattern perpendicular to groundwater flow
- Forms a long-lasting BioBarrier to intercept groundwater flow and prevent downgradient migration of COCs to the seeps
- BioBarrier consists of 72 injection points with a 10-foot spacing
- A total of 32,791 lbs of SRS was mixed with potable water to provide 20,000 gallons of solution for injection
- 197 lbs of yeast extract was added as a nutrient
- ~308 gallons of solution (35% of available pore volume) was injected at each point
- A target injection interval of 10-18 feet below ground surface was adjusted 10 feet deeper for a few points based on lithology
- Surfacing occurred at several injection points due to local lithologic variations

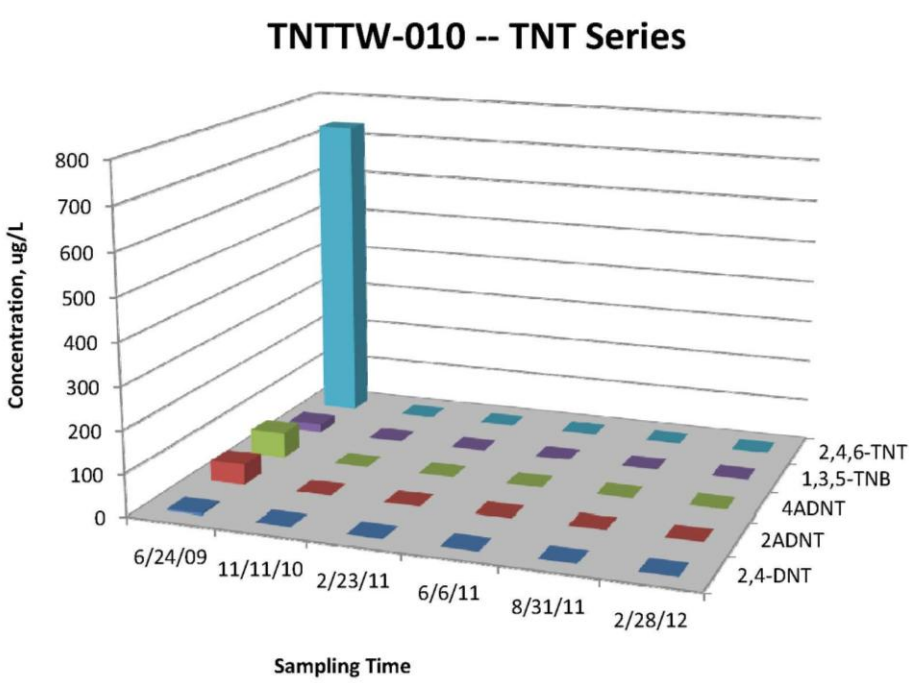
BioBarrier Layout

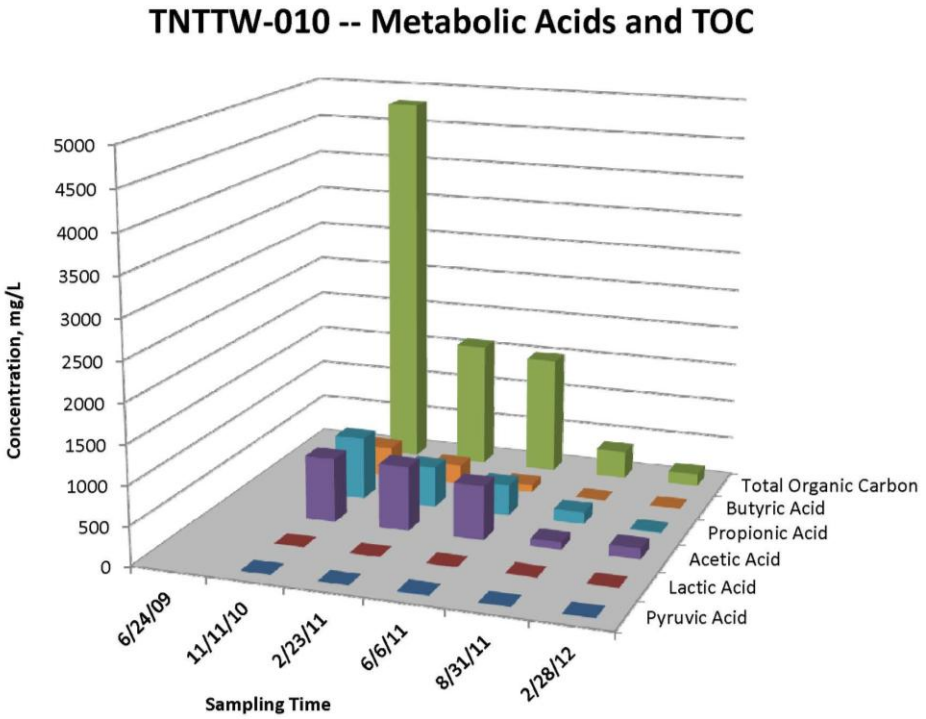


BioBarrier - SRS Mixing and Injection

SRS Injection for BioBarrier

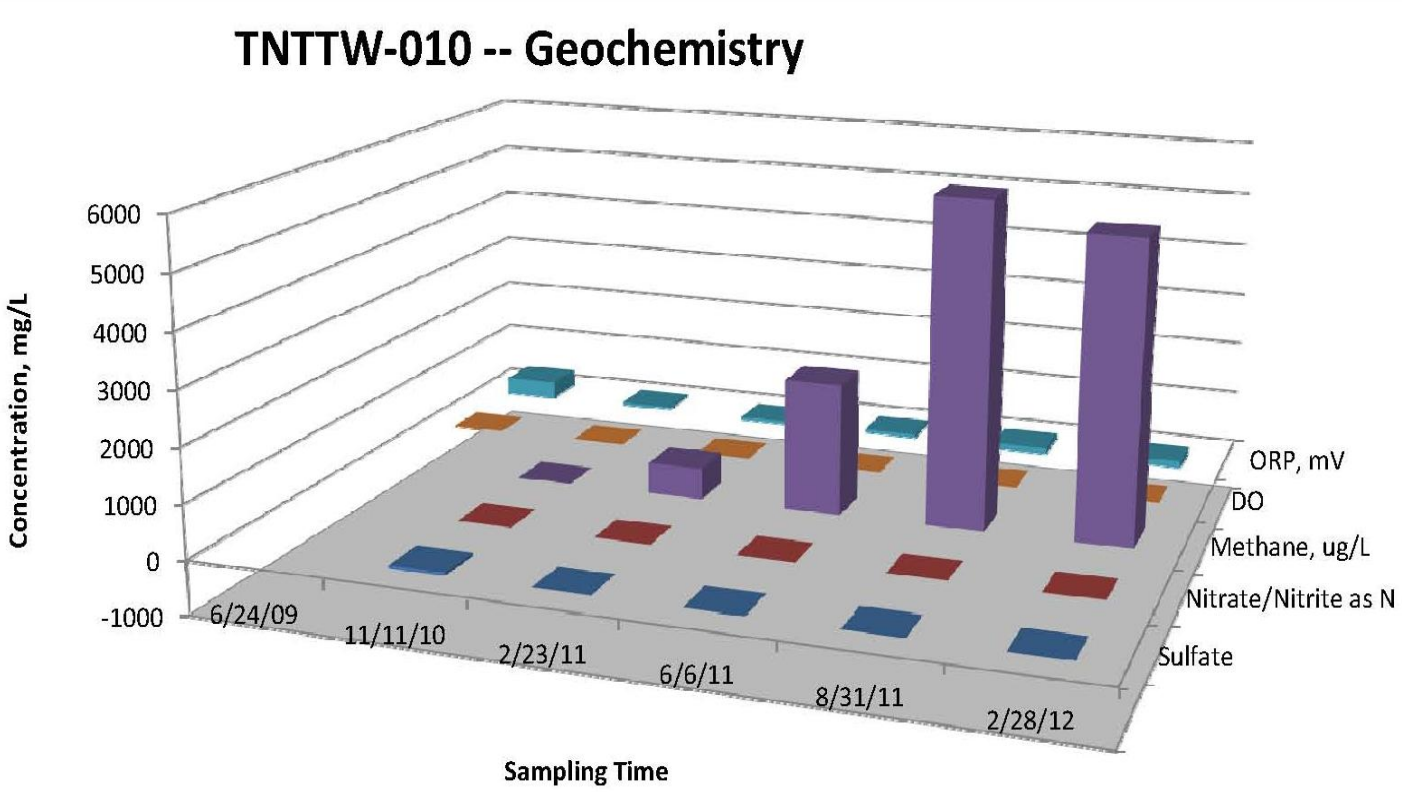
BioBarrier Results





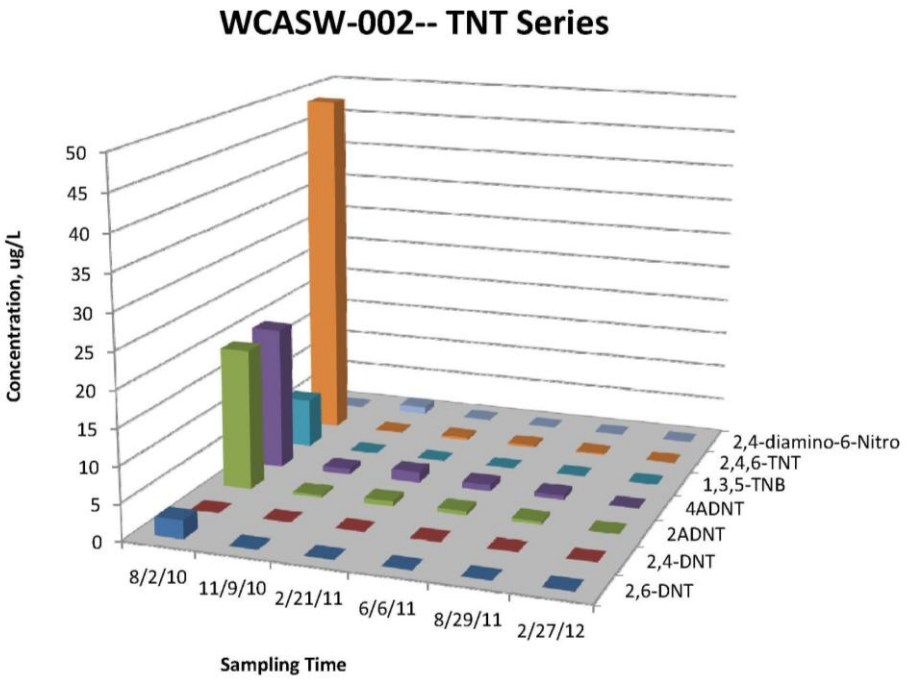
- TNT series compounds decreased to below detection limit of 20 ug/L three months after injection and has remained near non-detect
- TOC increased to 4,800 mg/L, and gradually decreased to 156 mg/L
- Metabolic acids increased to 820 mg/L, then decreased to ~100 mg/L

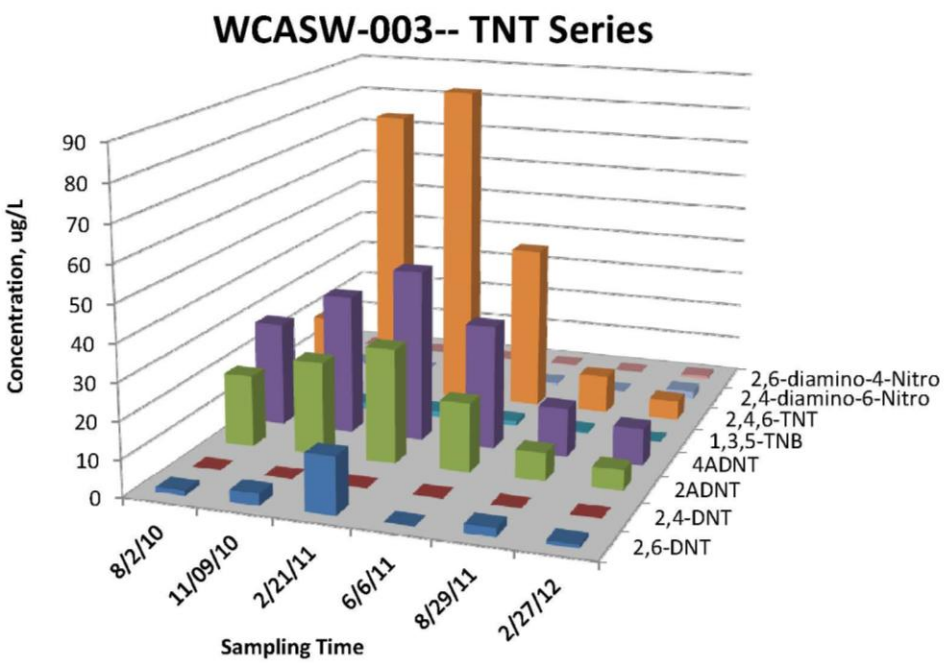
BioBarrier Results



- ORP dropped from 326.7 to -128.3 mV, then increased to -122.1 mV
- DO dropped from 9.7 to 0.72 mg/L
- Sulfate dropped from 59.9 to 1.2 mg/L
- Methane increased from 1.4 to 5,940 ug/L, then dropped to 5,480 ug/L

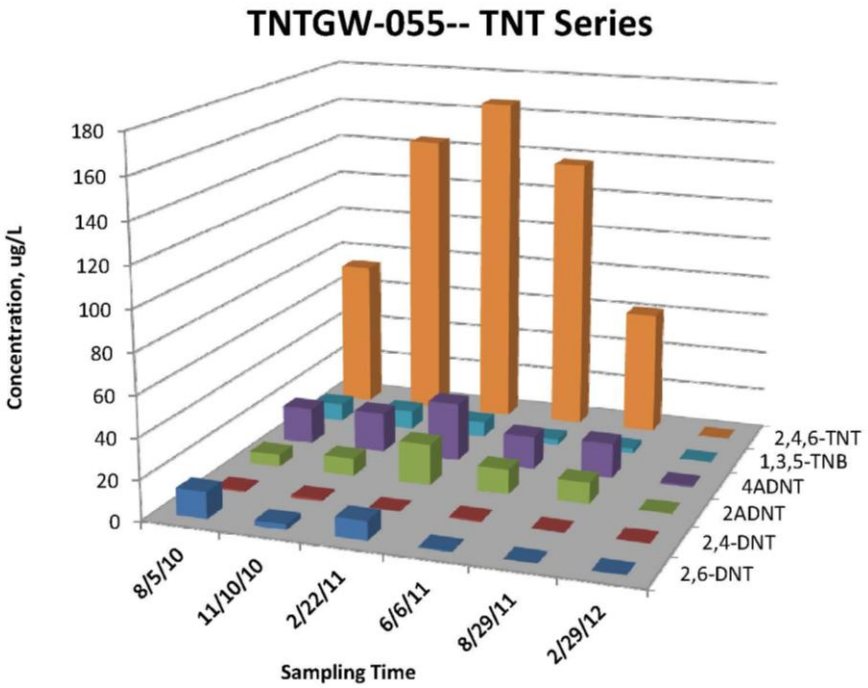
BioBarrier Results

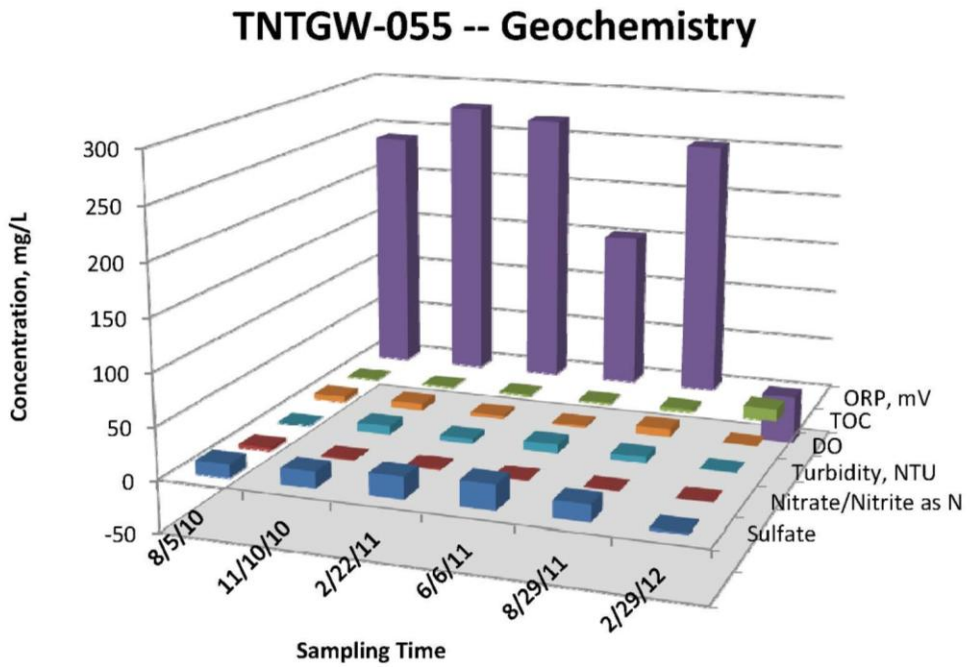




- More than 90% reduction of TNT series immediately downgradient at the seep location (WCASW-002)
- Further downgradient at seep location WCASW-003, initial increase in TNT series followed by a steady decrease
- No evidence of reducing conditions (i.e., no metabolic acids detected)

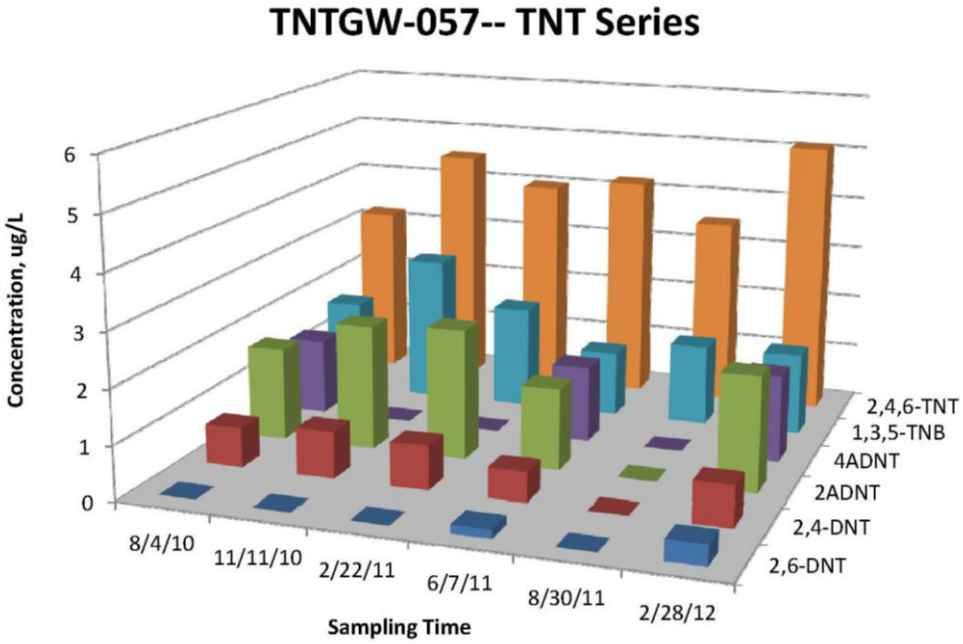
BioBarrier Results

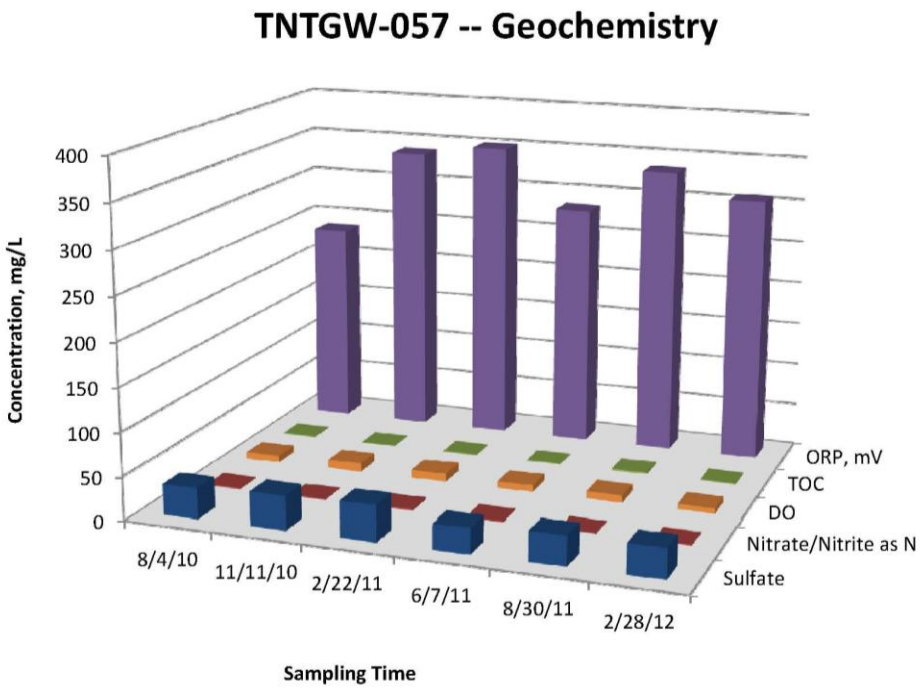




- TNT concentration increased from 73 ug/L to 166 ug/L then began a steady decrease to near non-detect
- Reducing conditions observed in 2/29/12 sampling with ORP dropping to -47.8 mV
- No metabolic acids detected

BioBarrier Results





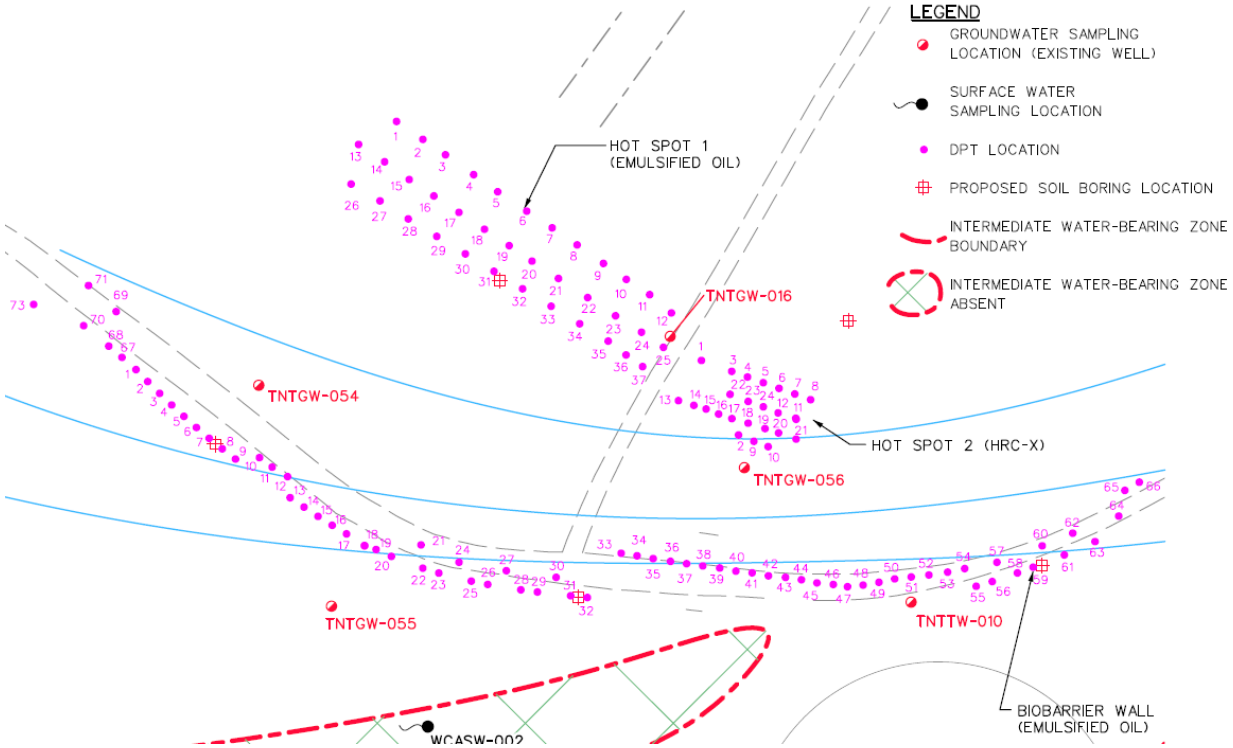
- Minor fluctuation in TNT Series at low concentrations
- No reducing conditions observed
- No metabolic acids detected

SE Hot Spot 1 Area

- SRS
- Located upgradient of the western portion of the BioBarrier
- High TNT concentration (156 ug/L), and relatively high groundwater flow rate (0.5 feet/day) → suitable for SRS
- A total of 17,867 lbs of SRS was mixed with potable water to provide 11,400 gallons of solution for injection at 37 points
- 107 lbs of yeast extract was added as a nutrient
- ~308 gallons of solution was injected at each point

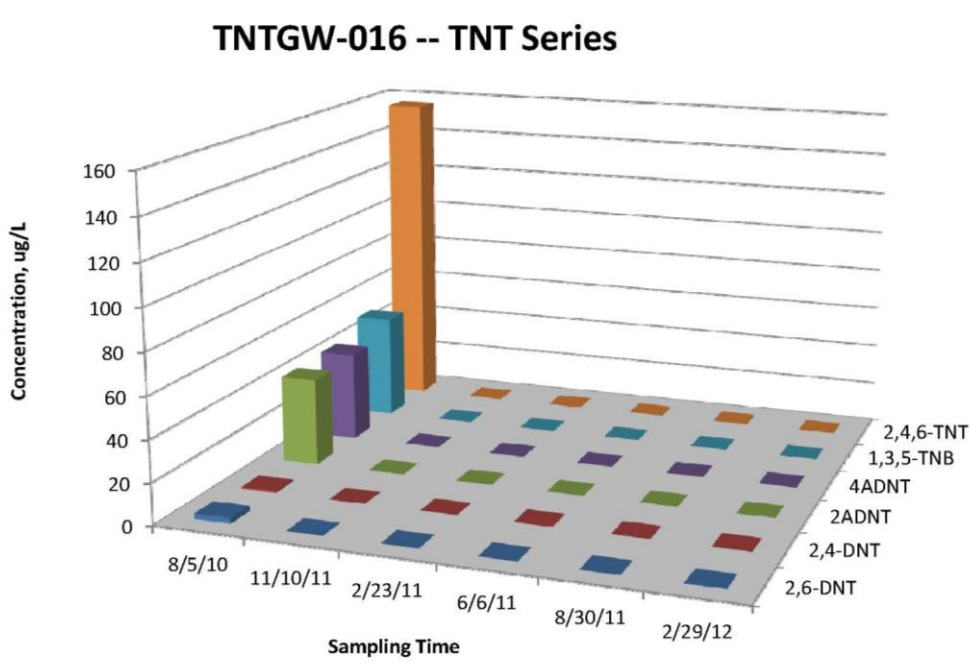
SE Hot Spot 1 Area

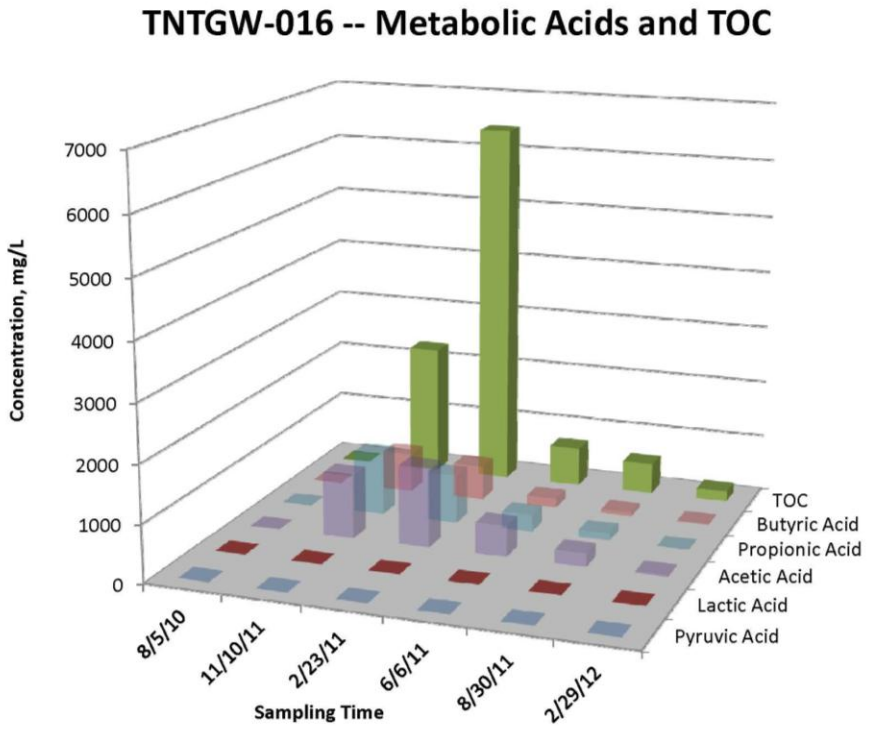
- 250-foot × 50-foot injection grid
- ~200 feet upgradient of the western portion of the BioBarrier (~ one year of groundwater travel time)
- Total of 37 injection points aligned in three parallel rows
- Target depth interval of 10-18 feet below ground surface, adjusted accordingly based on changes in elevation



SE Hot Spot 1 - SRS Mixing and Injection

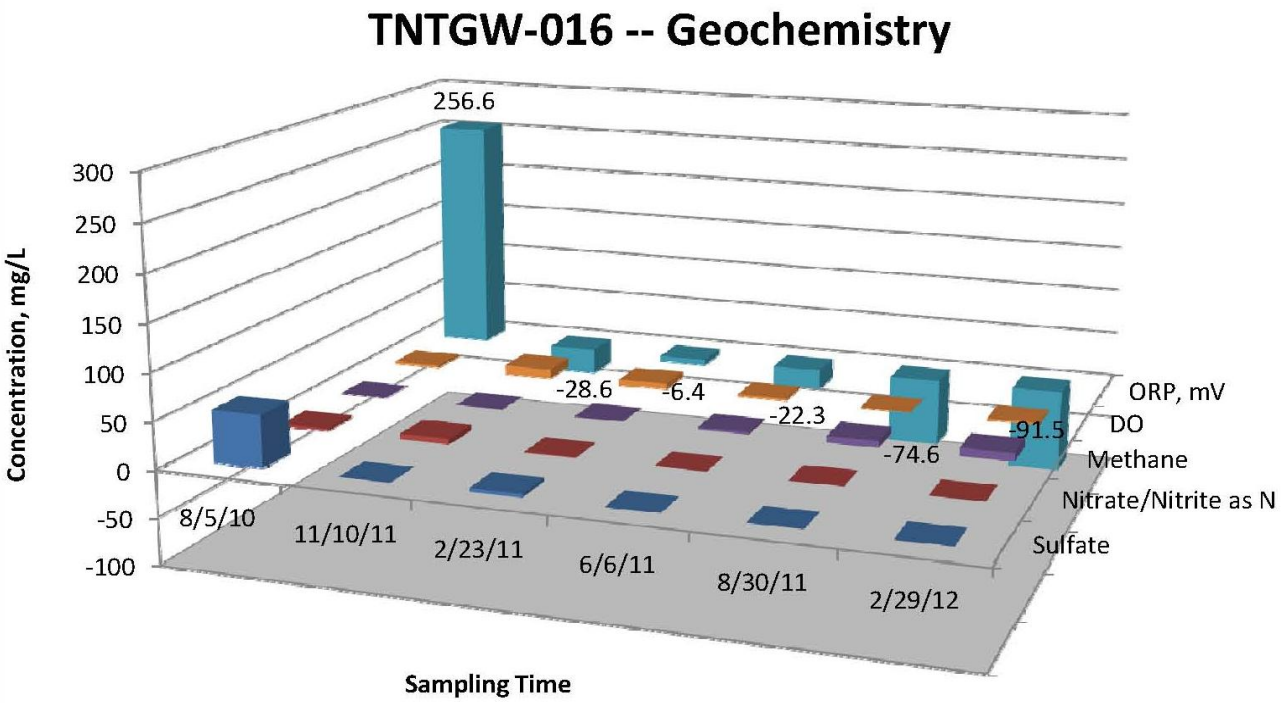
SE Hot Spot 1 Results





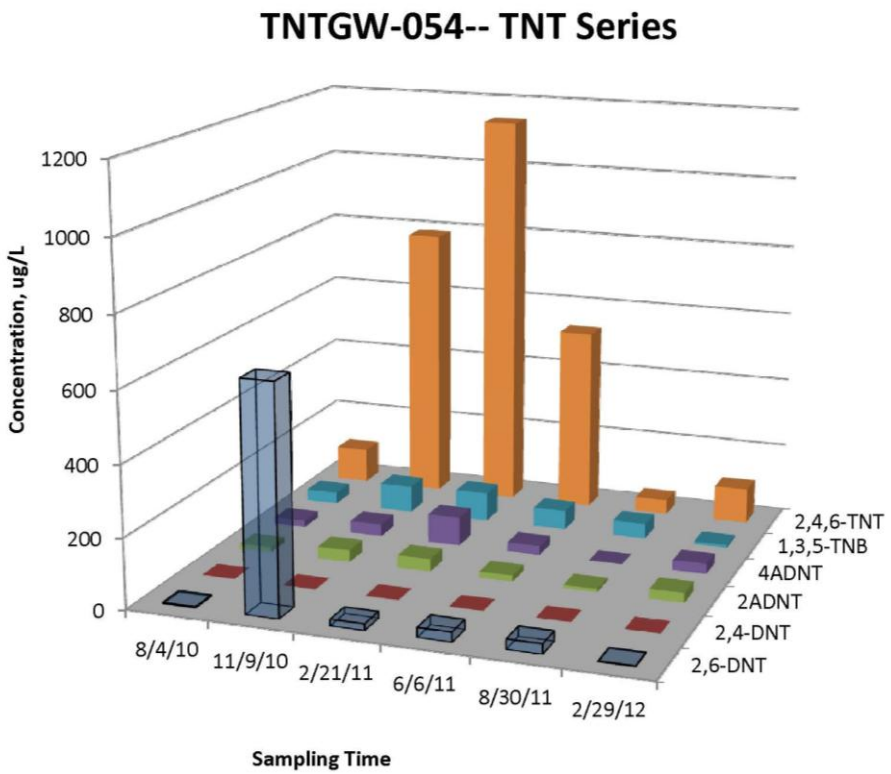
- TNT series concentration decreased to below detection limit of 20 ug/L three months after injection and has remained near non-detect
- Metabolic acids detected after 3 months and increased by 6 months then began to drop
- TOC peaked at 6,400 mg/L 6 months after injection then rapidly dropped

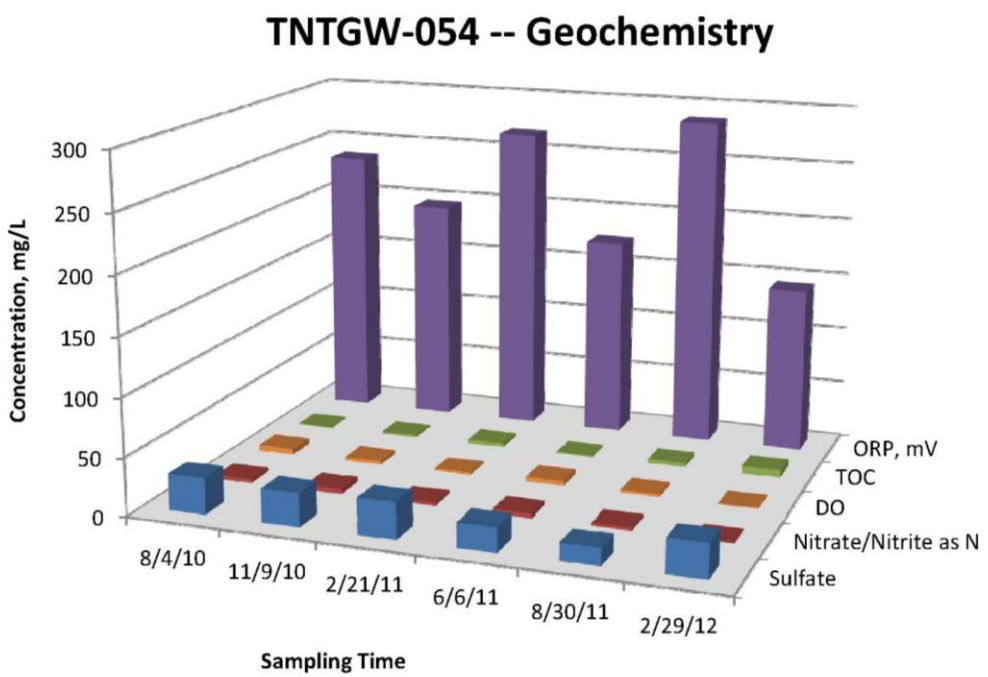
BioBarrier Results



- ORP decreased from 256.6 mV to -91.5mV
- Methane steadily increased to 8.88 mg/L (8,880 ug/L)
- Sulfate dropped from 55.3 mg/L to below the detection limit of 2 mg/L

SE Hot Spot 1 Results





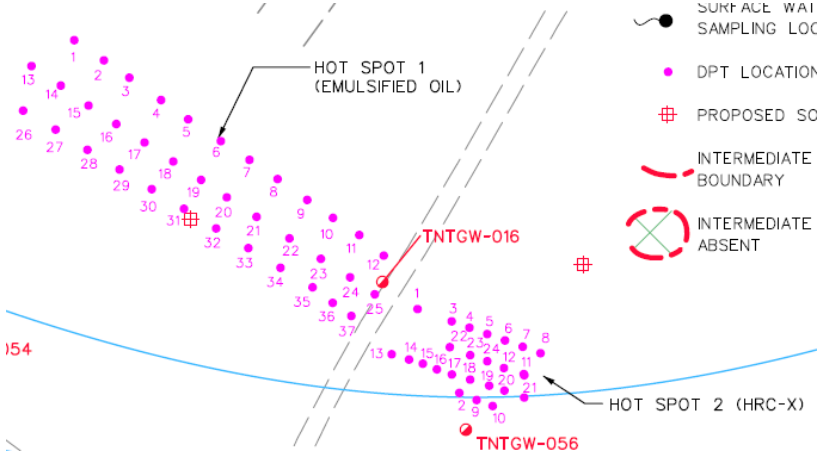
- TNT concentration increased from 99.8 ug/L to 1,140 ug/L 6 months after injection, dropped to 42.4 ug/L after 12 months, then increased to 102 ug/L after 18 months
- No metabolic acids detected until 18 months after injection when a small detection of Butyric acid was detected at 7.5 mg/L
- No significant TOC noted and no reducing conditions observed

SE Hot Spot 2 Area

- Located upgradient of the central portion of the BioBarrier
- High TNT concentration (156 ug/L) and relatively fast groundwater flow (0.5 feet/day)
- HRC-X selected for this area → side-by-side comparison with SRS (SE Hot Spot 1)
- A total of 810 lbs of HRC-X was injected through 24 points (~34 lbs for each point
- HRC-X was heated to 160 F in a hot water bath to reduce viscosity prior to injection; no dilution required

SE Hot Spot 2 - HRC-X Injection

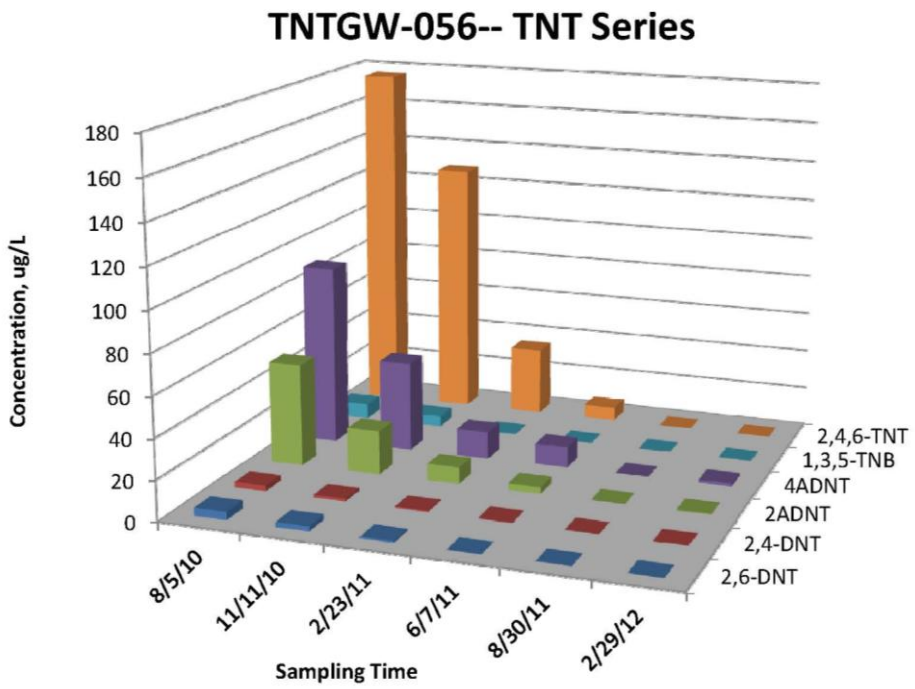
- A 100-foot × 50-foot injection grid
- ~180 feet upgradient of the BioBarrier (~ one year of groundwater travel time from SE Hot Spot 2 to BioBarrier)
- Total of 24 injection points spaced on 10-foot centers, aligned in four rows based on accessibility, in a staggered configuration
- Target depth interval of 3-8 feet below ground surface at the lowest elevation points, adjusted accordingly at higher elevations

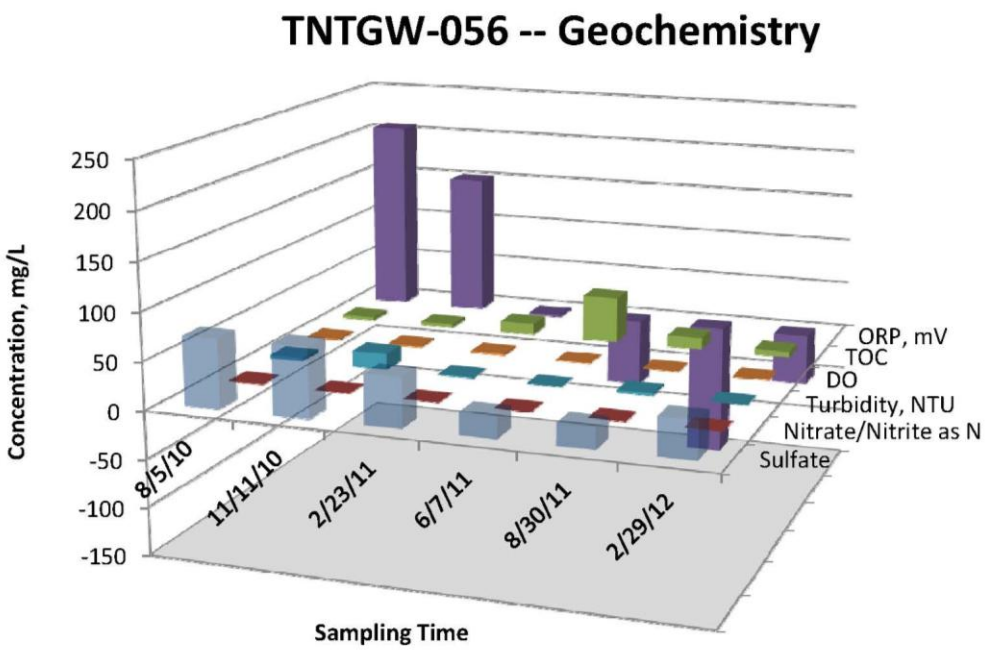


SE Hot Spot 2 – HRC-X Heating

SE Hot Spot 2 – HRC-X Injection

SE Hot Spot 2 Results





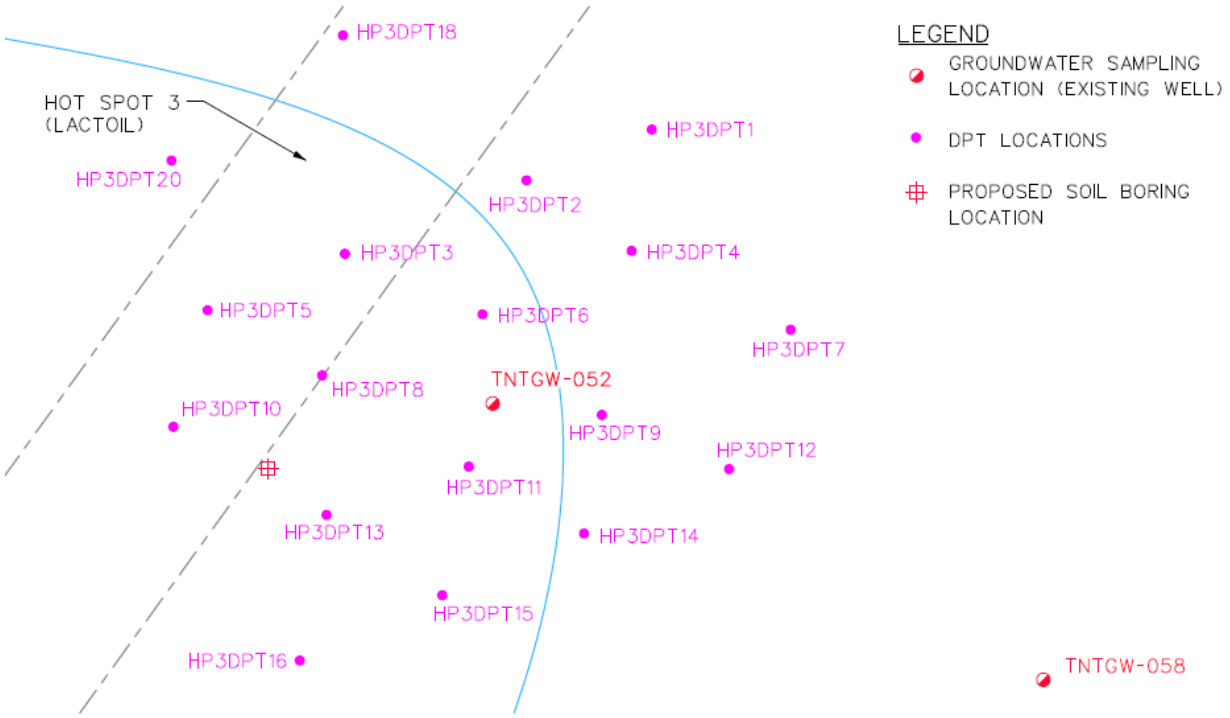
- Decrease in TNT from 176 ug/L to non-detect
- Steady decrease in ORP from 206.9 mV to -144.1 mV followed by a rebound to -54.6 mV
- Decrease in sulfate from 72 mg/L to 22.4 mg/L followed by a slight increase 38.7 mg/L

SE Hot Spot 3 Area - LactOil Injection

- Soil treatment (blending/removal) was conducted previously in this area
- Groundwater flow velocity 0.58 feet/day at nearby well TNTGW-019
- Relatively low TNT concentration (85 ug/L) – no critical requirement on carbon source longevity
- LactOil with relatively short life-span was selected as the carbon source
- A total of 5,714 lbs of LactOil was mixed with potable water to produce 3,500 gallons of solution for injection through 18 points (~200 gallons at each point)
- 34 lbs of yeast extract was added as a nutrient
- 300 lbs of $NaHCO_3$ added as a pH buffer

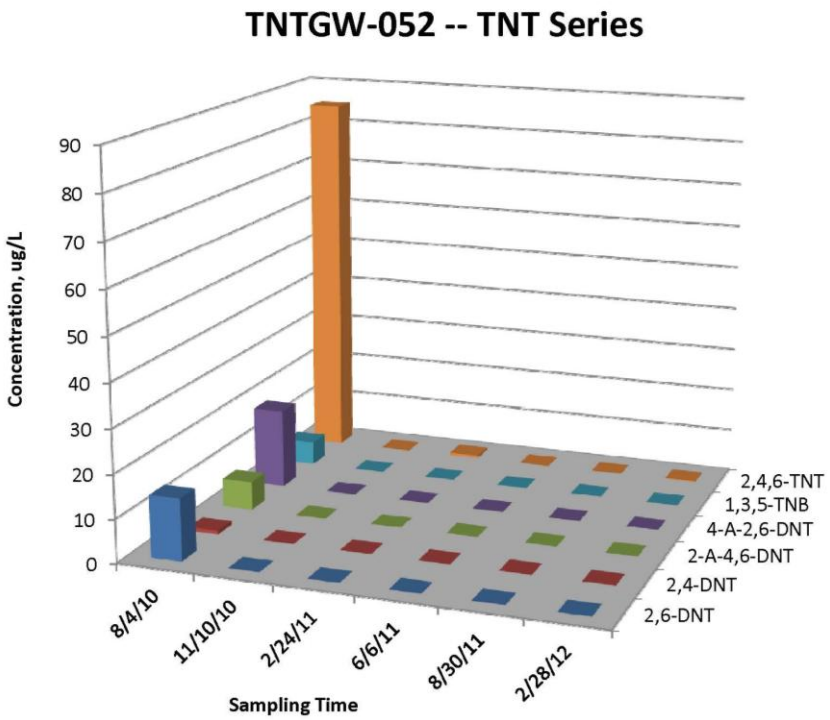
SE Hot Spot 3 Area

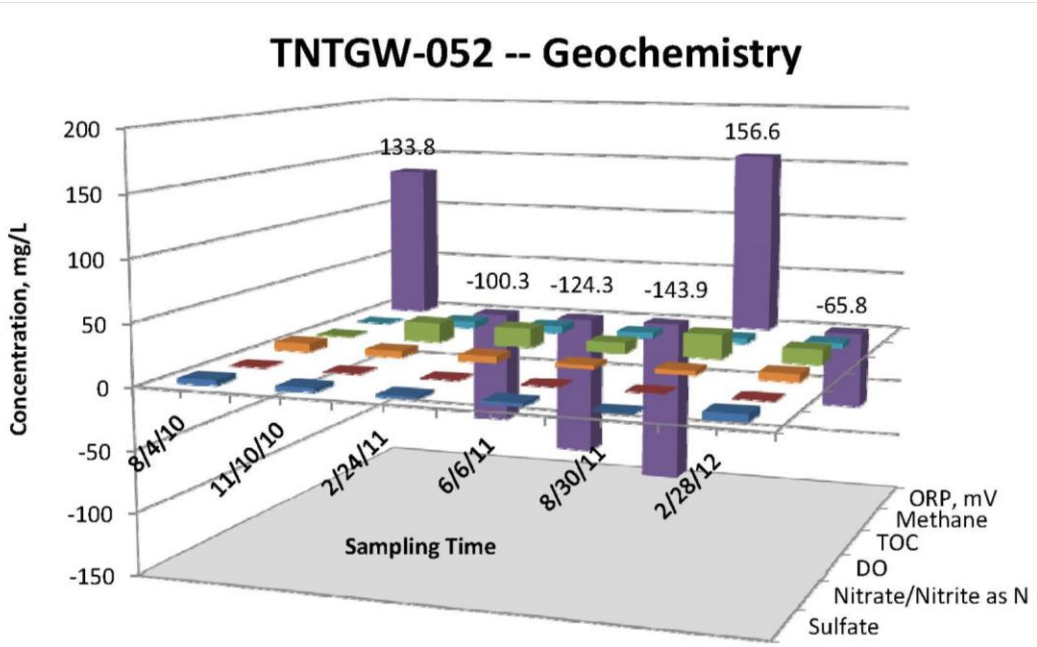
- A 80-foot × 80-foot injection grid
- Sixteen injection points in four staggered rows
- Due to surfacing at some points, two points were added in the field to achieve the design injection volume
- Target depth interval of 10-15 feet below ground surface at the lowest elevation points was adjusted accordingly at the higher elevation points



SE Hot Spot 3 - LactOil Injection

SE Hot Spot 3 Results





- TNT series concentration decreased to below detection limit of 0.20 ug/L three months after injection and has remained near non-detect
- ORP decreased for 9 months, spike upward, then decreased again
- TOC increased slightly
- No metabolic acids detected to date
- Methane increased to 6.24 mg/L (6,240 ug/L) and has remained above 4.5 mg/L (4,500 ug/L)

Comparing Performance

Parameters	SRS		HRC-X	LactOil
	TNTTW-010	TNTGW-016	TNTGW-056	TNTGW-052
Sulfate, mg/L	1.2	<1	22.4	2.1
Nitrate/Nitrite as N, mg/L	<0.05	<0.1	<0.05	< 0.05
Methane, µg/L	5,940	8,880	547	6,240
ORP, mV	-128.3	-91.5	-144.1	-143.9
DO, mg/L	0.72	0.57	0.46	3.46
TOC, mg/L	4,800	6,400	49.3	20.3
Pyruvic Acid, mg/L	10.9	< 1	< 0.1	< 0.1
Lactic Acid, mg/L	<10	< 10	< 1	< 1
Acetic Acid, mg/L	824	1,380	< 1	< 1
Propionic Acid, mg/L	797	1,080	< 1	< 1
Butyric Acid, mg/L	4,800	687	< 1	< 1

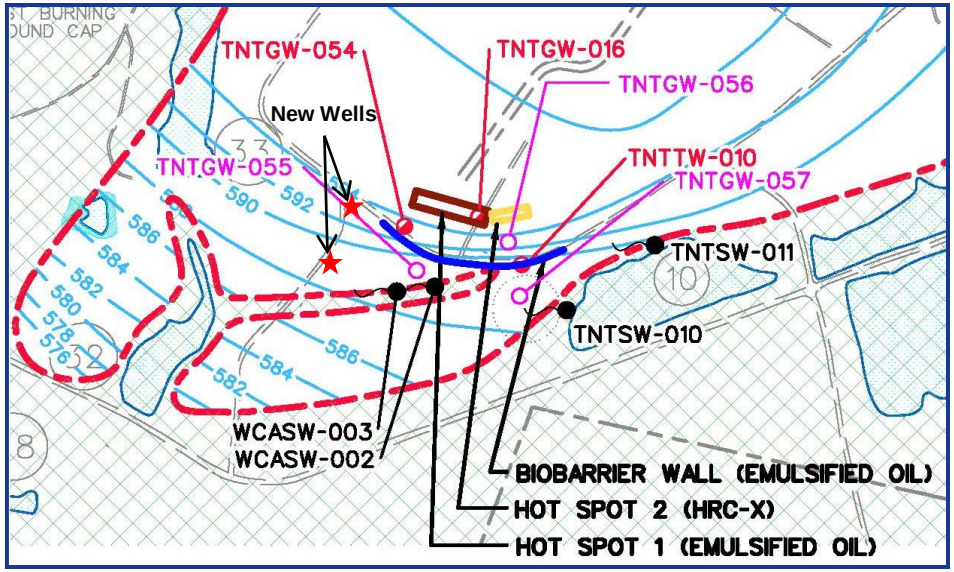
- Both SRS and LactOil decreased TNT series compounds to below detection limits within the injection grids
- Down-gradient of HRC-X injection grids showed a steady decrease of TNT series throughout the study
- All three substrates successfully created reductive conditions at the designed dosing rates
- LactOil generated a spike of methane and lowest ORP early on providing a short bloom of electron donors
- SRS generated two orders of magnitude higher TOC and metabolic acids – long-lasting slow release carbon source

Conclusion

- EISB is shown to be effective for treatment of groundwater contaminated with nitroaromatics
- Carbon source selection was based on several factors
  - Hydraulic gradient and groundwater flow velocity
  - Contaminant concentrations
- The designed dosing rates of carbon sources were able to create reducing conditions within the injection zones
  - Negative ORP values
  - Decreasing DO and sulfate
  - Increasing methane and metabolic acids
  - Contaminants decreased to below detection limits
- No downward trend in concentration observed downgradient of SRS injection area in the first two quarterly sample rounds
- Downward trend in concentration observed at the seep location nearest the BioBarrier, and down gradient of the HRC-X treatment area
- Pilot-scale field application provides valuable information for carbon source selection and full-scale design parameters

What Next?

- Install 2 new monitoring wells west of TNTGW-054 and TNTGW-055
- Collect baseline samples for new wells
- Inject HRC-X in target zone west of TNTGW-054
- Complete last semi-annual performance samples (including new wells)
- Collect two more rounds of performance samples from TNTGW-054, TNTGW-055, and two new wells



Questions?

Shaw® a world of Solutions™

CONTACT

Steven T. Downey, PE, PMP
Project Manager

865.694.7496
Steven.Downey@shawgrp.com